

A novel separation of the carbon types present in fly ash by density gradient centrifugation

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Introduction

The use of coal as a source of energy for both domestic and industrial use is a cost effective method for countries not supplied with hydropower or natural gas. However, pulverized coal combustion (PCC) furnaces (utility boilers) are associated with emissions of pollutants such as NO_x, SO_x, etc. The reduction in NO_x emissions, as dictated by Clean Air Regulations, has been addressed in PCC boilers by lowering the temperature of combustion, resulting in a lower combustion efficiency with a corresponding increase in the amount of unburned carbon in the ash. Fly ash is the principal by-product of coal combustion and its primary market in the US is as an extender in Portland cement. However, high-carbon fly ash is not suitable as a cement additive due to its tendency to adsorb the air-entrainment reagents, that must also be added to prevent crack formation and propagation. Consequently, the carbon rich ash is either placed in holding ponds or landfilled, thereby increasing the risk of leaching damages to the environment, raising disposal costs, and reducing revenue from ash sales.

Very little is known about the characteristics of the unburned carbon in fly ash and due to its significant impact, any information regarding the properties of these materials is being watched closely by the utility industry. Accordingly, the work reported here represents our initial efforts to isolate the unburned carbon in fly ash for subsequent examination. Three types of carbon particles have been identified microscopically: (i) inertinites, which appear to be particles that were rapidly entrained from the combustor prior to melting or combustion, and (ii) isotropic and (iii) anisotropic coke particles, that have passed through a molten stage while in the reactor. However, no isolation of these three carbon types has been conducted thus far. Since these carbon particles are generally of lower density than the inorganic matter in the fly ash and, in addition, the densities of the three types of carbon appear to differ, Density Gradient Centrifugation (DGC) is a suitable technique for simultaneously enriching these carbon types. This technique has been previously used to separate coal and kerogen macerals, but it has rarely been used to separate material with densities greater than $\sim 1.5 \text{ g/cm}^3$, due to limitations of the CsCl gradient media normally used. The results presented in this summary describe a DGC method for concentrating the three carbon types present in fly ash using a high density gradient media, that was prepared with polytungstate salts.

Separation methodology

Approximately 12 kg of fly ash were collected from the mechanical precipitators of a 70 MW boiler (Dale unit #3) operated by Eastern Kentucky Power. A series of preliminary enrichments were conducted to increase the amount of carbon in the ash and thereby, minimize the number of DGC runs required to accumulate sufficient sample for subsequent analyses. These steps included an initial screening of the sample with a 140 mesh sieve (106 μm), with the 140+ fraction being triboelectrostatically separated to obtain a sample with an inorganic matter content below 10 %.

A Beckman model J2-21 fitted with a 1.9 dm³ capacity titanium JCF-Z zonal core rotor was used for the DGC separations. A preliminary run was conducted on 10 g of the carbon enriched sample to ascertain the densities of the three carbon types and the level of purity that could be attained. Lithium heteropolytungstate (LST), which provides low-viscosity solutions to 2.85 g/cm³, was used to prepare the density gradients. For most runs, 7 density steps were employed, with the densities and volumes being tailored according to the densities targeted and varying from 1.20 g/cm³ to 2.25 g/cm³. In contrast to most prior DGC experiments on coal and kerogen macerals, no surfactant was used, since this material cannot be completely removed from the carbon particles and therefore could affect subsequent measurements, especially those related to adsorption properties. Loading and unloading of the sample and gradients were conducted at 1,500 RPM, with particle separations being conducted at 15,000 RPM (~ 22,500 g) for one hour. At the conclusion of the run, a 2.50 g/cm³ solution of LST was used to force the gradients out of the rotor and through a portable density meter to determine the collection cut points. The recovered fractions were then filtered, rinsed 3 times with deionised water, sonicated and dried overnight at ~50°C under 70-80 kPa vacuum.

Over 50% of the sample weight was recovered between 1.82-1.95 g/cm³, with various degrees of enrichment being observed for the three carbon types. As expected, the inorganic matter mostly partitioned (over 60%) to the densest fractions (> 2.3 g/cm³). Recovery of anisotropic coke maximized between 1.90-1.93 g/cm³, and reached a purity of ~71% compared to that of ~61% in the parent sample, with the primary impurities being isotropic coke. Isotropic carbons were concentrated in the density range between 1.73-1.76 g/cm³, intermediate to inertinites and anisotropic particles. Maximum purity was ~ 55%, notably higher than that of ~24% for the parent sample, with the main contaminant being anisotropic coke. Inertinites are the least dense carbon particles, maximizing between 1.54-1.62 g/cm³ with a maximum recovered purity of ~61%. This was considered an excellent enrichment as the inertinites only comprised ~6% of the parent sample. However, and contrary to expected, the primary impurities in these lightest fractions come from glass instead of carbon particles, due to an apparent entrapment of air in these inorganic materials.

The preliminary results demonstrate that it is possible to enrich the three carbon types present in fly ash by DGC. Future work will be directed at larger scale separations in order to accumulate sufficient material for characterization, including petrography, elemental analysis (both major and trace), thermogravimetric analysis and BET adsorption.

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